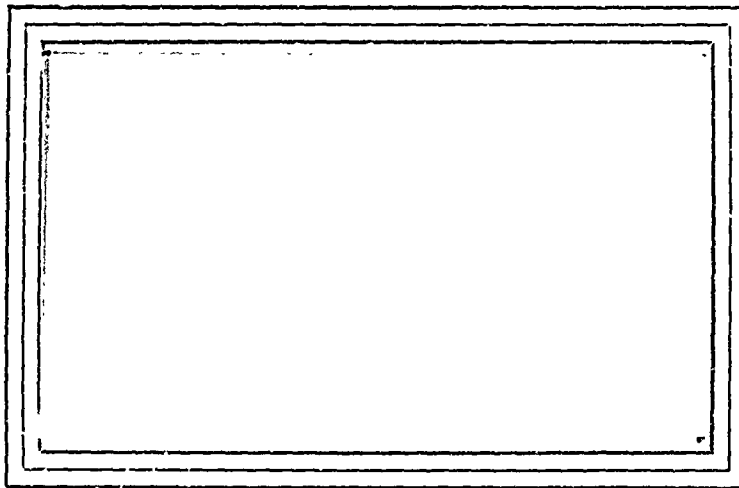


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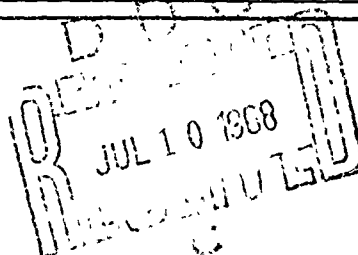
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RDTR No. 116

May 1968


STUDY OF GELLED ILLUMINANT COMPOSITIONS

by

R. M. Blunt
Denver Research Institute

This report was reviewed for adequacy and technical accuracy by
William E. Ripley

Released

A handwritten signature in cursive script, appearing to read "P. J. Smith".

P. J. Smith, Manager
Concept Development Division
Research and Development Department

UNCLASSIFIED

Final Report 3537-6805-F

STUDY OF GELLED ILLUMINANT COMPOSITIONS

Final Report

23 May 1967 - 23 May 1968

by

R. M. Blunt

Prepared Under Contract N00164-67-C-0498 for the Research & Development Department, U. S. Naval Ammunition Depot, Crane, Indiana, 47522, by the Mechanical Sciences and Environmental Engineering Division, Denver Research Institute, University of Denver, Denver, Colorado 80210

FOREWARD

This report summarizes and describes the work accomplished on Contract N00164-67-C-0498 during the period beginning June, 1967 and ending May, 1968 inclusive.

It is a pleasure to acknowledge the capable work of Mr. James Brewer and Mr. Robert Marchese on the tests and apparatus made during this study. Discussion of the program's objectives and problems with Mr. William Ripley of U. S. N. A. D.-Crane has been most helpful.

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I. ABSTRACT

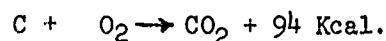
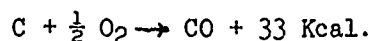
The high luminous intensity and color purity produced by the flames resulting from the combustion of Group II perchlorates with alcohol and other organic solvents had been noted in a 1966 study of air and water reactive materials (1). This present study was to investigate the feasibility of using these mixtures in markers, flares and similar devices or units that could be dropped from an aerial launching unit. The approach taken was that of characterizing the flame produced by a typical, operational device* in terms of size and candela. The intention was to show the improvement resulting from the addition of perchlorate-fuel gels to this flame, using a prototype of a device that might be added to existing markers of this type. It is concluded that a redesign of the marker would be necessary to take advantage of the properties of this particular gelled oxidizer/fuel combination. Data on gelling agents, Group II perchlorate solubilities in various organic liquids and flame color and candlepower are reported.

* (Marker, Location, Marine MK 2-0, Depth Charge, Night).

II. INTRODUCTION

In 1966 a study of air and water reactive materials was made with the object of improving the color purity and intensity of the flames produced by their reaction. Among the materials investigated as auxiliary components that might be used with the air and water reactives were solutions of alkaline earth perchlorates in methanol. These solutions were gelled by the addition of small amounts of "Carbopol 940" and the thickened material used as a colorant additive to an acetylene-air diffusion flame. It appeared that the intensity and purity of the visible radiation from the flame was much improved. It was postulated that the color purity of a flame containing hot solid particles is degraded by the continuum they radiate and suggested that the improved color purity was due, at least in part, to the removal of hot carbon from the acetylene diffusion flame. Although this flame depends upon the presence of hot carbon for its luminosity, it is actually relatively inefficient as a source of visible radiation. This may be estimated from the temperature, which in an air-acetylene pre-mix flame would not exceed 2200°C . For an optically thick flame, black-body conditions may be assumed as an approximation and by appropriate calculations the ratio of the visible power to the total power radiated found to be 3.5%.* By replacing this radiator with one which is more selective, i. e., which radiates as much as possible in the 0.4 micron to 0.7 micron region and a minimum elsewhere in the visible spectrum, a much higher efficiency can be obtained. Actually, the flames used in this study are diffusion flames which would exhibit even lower temperatures and efficiencies.

The addition of a perchlorate-rich gel to a luminous carbon flame of this type was expected to increase the oxygen available to the reaction as a result of the decomposition of the perchlorates. The effect may be very similar to that produced when oxygen gas is pre-mixed with the acetylene as in the common welding torch; the free carbon is replaced by CO and CO_2 . At the same time an increase in the flame temperature would be expected from the reactions



going more nearly to completion.

The removal of solid carbon from the flame and the increase in temperature would produce a hotter flame, but one that would be

* This does not consider conversion losses in the utilization of the reactants, which result in a lower over-all efficiency.

less luminous unless the higher temperature were used to excite a more effective radiation source.

By good fortune, the perchlorates that are most soluble in common organic solvents include those of sodium, barium and strontium, because these are also metals which produce efficient visible-region radiators in the form of Na, BaO, BaCl, Sr Cl, etc., which in turn are just those products one expects to find from the decomposition of the perchlorate. The decomposition of these perchlorates may be accompanied by the release of considerable heat, up to the order of 100 Kcal/mol, which is also a desirable effect. Thus, the removal of solid carbon particle radiators by oxidation to CO or CO₂, the increase in flame temperature due to this process as well as to the decomposition of the perchlorate and the simultaneous presence of desirable radiating species would all work together to make the alcohol-perchlorate type of mixture desirable as an additive modification to devices such as the Marker, Marine, MK 2-0.

The present study was conducted to broaden the base of information concerning the possible combinations of perchlorates, solvents and gelling agents in the hope of finding a better combination than that used in the previous work, which was the methanol-carbopol-perchlorate one. This search was followed by a short study of the characteristics of the most promising combinations as to ease of ignition, combustion phenomena, flame color, purity and spectral distribution. Those selected were tested in conjunction with a semi-prototype device. This device was to provide a means of injecting these gels into the flame from a Marker, Marine, MK 2-0 in order that a judgment of the effectiveness of this application could be made. The details of the experimentation are reported in Section III.

III. EXPERIMENTAL WORK

Work was initiated with a survey of the commercially available gelling agents that seemingly could be used in conjunction with organic solvents such as alcohols, ketones, amines and hydrocarbons. From this survey, the following materials were selected for trial. Other agents, far too numerous to permit the testing of each one, could have been selected. Subject to the requirement that gels be produced from the largest possible number of prospective organic fuels, the following choices were made on the basis of availability of data and material.

"Duponol" G is an amine salt of a saturated long-chain alcohol sulfate. It has excellent surface active properties in aqueous solution but is primarily employed as an oil and wax soluble emulsifying agent. Solubility is good in alcohols, ketones, aromatic and aliphatic hydrocarbons and water. It is a duPont product.

"Alkanol" is also a duPont product and is formed by the condensation of a higher fatty alcohol with ethylene oxide. It is soluble in water, alcohols, ketones and aromatic hydrocarbons in concentrations from one per cent to 10 per cent and to a lesser extent in kerosene. It is stable in the presence of heavy metal ions.

Zelec NK is a fatty alcohol phosphate very soluble in ethyl alcohol, ethyl acetate, xylene, benzenes, etc., and to some extent in water.

"Carbopol" is a Goodrich Chemical Co. product based on carboxy-vinyl polymers of high molecular weight. The "940" type appears best suited to the requirements of this program. It is useful with gasoline, kerosene, methanol, ethanol, ketones, etc., even though it is not soluble in all of these liquids.

The study which led to this investigation used methanol as the solvent fuel and "Carbopol" as the gelling agent. The manufacturer recommends neutralizing the "Carbopol" solution with a base such as triethylamine or ammonium hydroxide to produce a gel. The best gels, however, were obtained from perchlorate-alcohol solutions when no neutralization was done.

Oxidants that were of interest for the purposes of this investigation should be soluble in the fuel liquids. While it is not essential that the oxidizer dissolve readily in the fuel, it does help in the preparation of a smooth gel if a high degree of solubility exists. In addition, clogging of small orifices used to inject the gel into a flame is minimized. Oxidants that are essentially

insoluble in the fuel could be used but the gel would serve mainly to suspend them in an even distribution through the material as well as to provide some control over the viscosity of the mixture.

Only perchlorates were used as the oxidants in the earlier work, because of the high oxygen content of these compounds and the high solubility of alkali or alkaline earth perchlorates in alcohol. The current study included some of the first and second group nitrates in addition to the perchlorates. These were soon eliminated by the poor performance, i. e., poor ignition, combustion and color production, in addition to their insolubility.

The intense green radiated from the flame during the combustion of boron or boron compounds requires relatively high flame temperatures to produce the desired color and intensity. This flame may be a good source to use as a green signal flare and for this reason an attempt to use methyl borate and barium perchlorate in gelled methanol was made, but it did not produce good results. Further work on boron compounds was not pursued. From the data available, more should be done with this element as a flame colorant than the limitations of the present study permitted.

With the above considerations in mind, it appeared most desirable to screen the materials that were available to select those which would merit further work. The following summary shows what was done. In this series of tests, small quantities of mix were prepared to determine the general mechanical characteristics, such as consistency, color, handling problems and the burning rate type of burn, flame color and intensity. Properties of the fuels and oxidizers are listed in Table 1 and Table 2, respectively. The compositions are listed in Table 3 with an identifying serial number and a short note summarizing the observations on mechanical and burning properties.

The observations noted in Table 3 narrowed the choice of compositions to thirteen. From an inspection of these, compositions based on methyl alcohol, trimethyl borate and kerosene as fuels, with sodium, barium or strontium perchlorate as oxidizers and Zelec or Carbopol as the gelling agent, appeared most likely to be useful. The following 8 compositions were finally selected to test for candlepower, dominant wavelength and color purity and eventual trial in the MK 2-0 burner adapter prototype.

- 1) Na-1: NaClO_4 , 60 gms; CH_3OH , 30 ml; Zelec, 20 gms.
- 2) Na-2: NaClO_4 , 50 gms; Kerosene, 31 ml; Zelec, 20 gms.
- 3) K -1: KClO_4 , 55 gms; CH_3OH , 40 ml; Carbopol, 6 gms.
- 4) K -2: KClO_4 , 54 gms; Kerosene, 36 ml; Carbopol, 10 gms.
- 5) Ba-1: $\text{Ba}(\text{ClO}_4)_2$, 74 gms; CH_3OH , 30 ml; Carbopol, 3 gms.
- 6) Ba-2: $\text{Ba}(\text{ClO}_4)_2$, 51 gms; Kerosene, 33 ml; Zelec, 17 gms.
- 7) Sr-1: $\text{Sr}(\text{ClO}_4)_2$, 76 gms; CH_3OH , 14 ml; Zelec, 13 gms.
- 8) Sr-2: $\text{Sr}(\text{ClO}_4)_2$, 63 gms; Kerosene, 25 ml; Zelec, 13 gms.

TABLE 1. OXIDANT CANDIDATES

Formula	Approx. Weight % of O ₂	CH ₃ OH	C ₂ H ₅ OH (Solubility, grams per 100 grams solvent at approximately 20° C.)	(CH ₃) ₂ CO	C ₅ H ₅ N (2)	(C ₂ H ₅) ₂ O (3)	Cello- solve	Refer- ence
Ba(ClO ₄) ₂	38	68.46	55.48	55.49	-	-	107.56 <u>a</u>	1 a
Ba(NO ₃) ₂	37	0.06	0.002	0.01	-	-	-	1 b
Ca(ClO ₄) ₂	54	70.36	62.44	38.18	-	0.26	-	1 c
Ca(NO ₃) ₂	59	144.2	51.4	16.8	5.83	-	33.2 <u>b</u> 58.4 <u>c</u>	1 d
LiNO ₃	70	-	-	3.00	27.76	0.09	-	2 a
LiClO ₄	60	182.2	151.8	136.5	-	113.7	-	3, 4
Sr(ClO ₄) ₂	45	67.95	64.37	150.06	-	-	-	2 b
Sr(NO ₃) ₂	45	-	0.02	-	0.710	-	1.66 <u>b</u> 0.05 <u>c</u> 0.02 <u>c</u>	2 c
NaClO ₄	52	34.33	12.87	34.10	-	-	-	2 d
NaNO ₃	56	0.41	0.04	1.98 <u>d</u>	0.35	-	-	2 e

a - ethyl cellosolve
b - methyl cellosolve
c - butyl cellosolve
d - 90% wt. acetone in solvent

(1) Dioxane 1, 4
 (2) Pyridine
 (3) Diethyl ether (ether)

TABLE 2. ORGANIC FUEL CANDIDATES

Name	Formula	Mol.Wt.	B.P., °C	d, g/cm ³	Reference
Methanol	CH ₃ OH	32	64	0.79	6e
Ethanol	C ₂ H ₅ OH	46	78	0.78	6f
Propanol	CH ₃ (CH ₂)OH	60	97	0.80	6f
Acetone	CH ₃ ·CO·CH ₃	58	56	0.78	6g
M. E. K.	CH ₃ ·CO·C ₂ H ₅	72	79	0.81	6g
Benzene	C ₆ H ₆	78	80	0.87	7e
Toluene	C ₆ H ₅ CH ₃	92	110	0.87	6a
n-Pentane	CH ₃ (CH ₂) ₃ CH ₃	72	36	0.62	7c
n-Hexane	CH ₃ (CH ₂) ₄ · CH ₃		68	0.65	7d
Petrol- eum ether	Fraction petro- leum Benzine (mainly hexane)		40 - 60	0.63	6c
			27 - 58	0.63	7b
Benzine	Fraction petro- leum Benzine (heavy)		100 150	0.75	6d
Diethyl- amine	(C ₂ H ₅) ₂ NH	73	56	0.71	7f
Triethyl- amine	(C ₂ H ₅) ₃ N	101	90	0.73	7f
Pyridine	C ₅ H ₅ N	79	115	0.97	7g
Kerosene			100-250	0.81	7a
1, 4 Dioxane	C ₄ H ₈ O ₂	88	101.2 101.4	1.03	6h

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	1	2	3	4	5	6	7	8
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂	4.41	6.3	1.6	4.7	4.0	4.9	3.4	7.2
Sr(ClO ₄) ₂								
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan				4.0	1.8			
Acetone								
Methanol						10.2	2.4	2.8
Ethanol	8.2	8.5	11.1					
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane								
Kerosene								
Mineral Spirits								
Duponol G								
Carbopol 940								
Zelec NK	8	4.0	2.2	0.9	.02	5.0	1.4	1.2
Alkanol HCS								
Hexaglycerol-disoyaester								
REMARKS:								
Ignition	Good	good	good	good	good	good	good	good
Propagation	Spora-dic	Spora-dic	Spora-dic	spora-dic	contin-uous	spora-dic	spora-dic	nearly steady
Color Purity	weak grn/wh	stronger grn/wh	poor green wht	good green white	poor green	gd grn + wht	better green	intense green
Color Intensity								
Viscosity								
Appearance	white paste	white paste	white paste	white solid	wh paste & solid	white solid	white paste	lt/yel paste
Candidate ?	no	no	no	maybe	no	no	no	maybe

TABLE 3. COMPOSITIONS

Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	9	10	11	12	13	14	15	16
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂	3.0	5.9	4.3	3.3	4.2	6.8	4.8	
Sr(ClO ₄) ₂								5.8
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan	2.3							
Acetone		2.6	2.2					
Methanol	2.4							1.1
Ethanol								
Pyridine								
Triethyl Amine					2.8	3.4	1.9	
Diethyl Amine								
Hexane								
Kerosene								
Mineral Spirits								
Duponol G				0.5				
Carbopol 940	0.03	0.2				0.1		0.3
Zelec NK								
Alkanol HCS			0.5		0.4			
Hexaglycerol-disoyaester								
REMARKS:								
Ignition	Good	Good	Good	Good	Good	Good	Good	Good
Propagation	stable	stable	stable	stable	sporadic	stable	stable	stable
Color Purity	good green	gd/grn in-tense	red turns green	see 11	grn in flame	red then to green	red to brt/grn	deep red
Color Intensity								
Viscosity								
Appearance	white solid	lt/yel paste	lt/yel paste	lt/yel paste	lt/yel paste	white paste	white paste	white paste
Candidate ?	no	maybe	no	no	maybe	no	no	maybe

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	17	18	19	20	21	22	23	24
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂								
Sr(ClO ₄) ₂	5.6	8.6	7.8	6.7				
Li(ClO ₄) ₂						4.5	3.9	6.8
Trimethylborate								
Dioxan				9.0				
Acetone		2.2	2.4					
Methanol	1.0					2.1	1.7	
Ethanol								2.3
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane								
Kerosene								
Mineral Spirits								
Duponol G		0.5						
Carbopol 940						0.2		
Zelec NK	0.6		0.5				0.4	1.2
Alkanol HCS								
Hexaglycerol-discyaester								
REMARKS:								
Ignition	fair	fair	fair	good	poor	poor	poor	poor
Propagation	stable	stable	stable	stable	stable	doesnt sustain	doesnt sustain	doesnt sustain
Color Purity	deep red	deep red	deep red	deep red	no red	little or no	little or no	little or no
Color Intensity								
Viscosity								
Appearance	lt/yell paste	lt/yell paste	lt/yell paste	wht. thick paste	gran. gel	white paste	white paste	white paste
Candidate ?	no	no	no	maybe	no	no	no	no

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	25	26	27	28	29	30	31	55
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂								3.7
Sr(ClO ₄) ₂								
Li(ClO ₄) ₂	4.3	8.3	5.0	4.3	4.4	4.8	3.5	
Trimethylborate								1.0
Dioxan	8.4	2.4	1.0				1.0	
Acetone				1.2	1.4			
Methanol								1.3
Ethanol		2.1	1.4					
Pyridine								
Triethyl Amine						9.6	1.0	
Diethyl Amine								
Hexane								
Kerosene								
Mineral Spirits								
DuPont G				0.5				
Carbopol 940	0.2	0.3						0.2
Zelex NK			0.7		0.9		0.9	
Alkanol HCS								
Hexaglycerol-disoester								
REMARKS:								
Ignition	good	good	fair	fair	fair	good	poor	easy
Propagation	stable	stable	stable	stable	stable	stable	poor	flashes
Color Purity	poor red	improved	as 26	pale red	pale red	color less	poor	good
Color Intensity								good
Viscosity								paste
Appearance	white solid	lt/yel solid	yellow solid soft	lt/yel paste	yellow paste	wht thick paste	white paste	white
Candidate ?	no	no	no	no	no	no	no	maybe

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	56	66	67	68	69	70	71	72
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂	0.8	2.5	2.5		1.8			
Sr(ClO ₄) ₂			2.0	3.4				2.2
Li(ClO ₄) ₂						2.3		
Trimethylborate	2.2	2.8						
Dioxan								
Acetone								
Methanol	0.9							
Ethanol		2.8	2.0					
Pyridine				2.0	1.1	3.5		
Triethyl Amine								
Diethyl Amine							1.6	2.5
Hexane								
Kerosene								
Mineral Spirits								
Duponol G								
Carbopol 940			0.3					
Zelec NK	0.5	0.4					0.7	0.6
Alkanol HCS								
Hexaglycerol-disoyaester								
REMARKS:								
Ignition	easy	easy	easy	easy	easy	easy	easy	easy
Propagation	fair	fair	good	pul- ses	fair	cons- istent	fla- shes	puls- es
Color Purity	fair	poor	good	poor	poor	poor	poor	poor
Color Intensity	varies	good	good	good	good	weak	weak	fair
Viscosity	liquid	solid	paste	paste	paste	low	paste	paste
Appearance	yel- low	white	white	white	white		yel- low	yel- low
Candidate ?	maybe	maybe	maybe	n.g.	n.g.	n.g.	n.g.	n.g.

TABLE 3. COMPOSITIONS

Solvent as ML, Oxidant & Gelling Agent Weight in Grams

Test Serial No.	73	74	75	76	77	78	79	80
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂	3.6	1.7	2.0	1.8	1.6	1.6		
Sr(ClO ₄) ₂							1.8	2.1
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan								
Acetone								
Methanol								
Ethanol								
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane	3.5	1.0	1.1	1.7				
Kerosene					1.0	0.6	0.7	0.8
Mineral Spirits								
Duponol G			0.8			0.7		0.5
Carbonol 940		0.4						
Zelec NK								0.5
Alkanol HCS								
Hexaglycerol-disoyaester		0.5		0.8	0.5		0.4	
REMARKS:								
Ignition	easy	easy	easy	easy	easy	fair	easy	easy
Propagation	flashes	flashes	flashes	pulses	pulses	unsteady	flashes	flashes
Color Purity	poor	poor	poor	poor	poor	poor	poor	poor
Color Intensity	fair	fair	fair	strng	strng	strng	strng	strng
Viscosity	paste	paste	paste	paste	liquid	paste	paste	paste
Appearance	yellow	white	yellow	white	white	yellow	white	white
Candidate ?	n.g.	n.g.	n.g.	ng	n.g.	n.g.	n.g.	n.g.

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	81	82	83	84	85	86	87	88
KClO ₄								
NaClO ₄								
Ba(ClO ₄) ₂						1.3	1.7	1.6
Sr(ClO ₄) ₂	2.5	1.4	1.7	1.3	1.35			
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan								
Acetone								
Methanol								
Ethanol								
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane		1.0	1.2	1.2	1.4			
Kerosene	1.0							
Mineral Spirits						2.2	2.8	2.0
Duponol G			0.8				0.6	
Carbopol 940								
Zelec NK	0.5				0.4	0.4		
Alkanol HCS								
Hexaglycerol-disoyaester		0.8		0.6				0.5
REMARKS:								
Ignition	easy	easy	easy	easy	easy	easy	easy	easy
Propagation	smooth	flashes	flashes	poor	pulses	poor	better	good
Color Purity	poor	poor	poor	poor	poor	poor	poor	poor
Color Intensity	strng	strng	weak	weak	strng	strng	strng	good
Viscosity	paste	sticky	paste	sticky	paste	paste	paste	paste
Appearance	white	yellow	yellow	yellow	white	white	white	white
Candidate ?	n.g.	n.g.	n.g.	n.g.	maybe	n.g.	maybe	maybe

TABLE 3. COMPOSITIONS

Solvent as ML, Oxidant & Gelling Agent Weight in Grams

Test Serial No.	91	92	93	94	95	96	97	98
KClO ₄		1.7	1.9	1.9	2.0	3.2	1.4	
NaClO ₄								1.8
Ba(ClO ₄) ₂								
Sr(ClO ₄) ₂	1.5							
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan								
Acetone		1.1	1.2	1.4				
Methanol						2.1	1.2	0.8
Ethanol					1.8			
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane								
Kerosene								
Mineral Spirits	1.2							
Duponol G	0.7							
Carbopol 940								
Zelec NK		0.5	0.3			0.4		0.6
Alkanol HCS				0.5	0.5			
Hexaglycerol-disoyaester							0.3	
REMARKS:								
Ignition	easy	easy	easy	easy	easy	poor	poor	good
Propagation	fair	irreg	irreg	poor	irreg	poor	poor	good
Color Purity	poor	fair	fair	poor	poor	poor	poor	fair
Color Intensity	strng	fair	fair	poor	strng	weak	weak	strng
Viscosity	paste	paste	paste	paste	paste	paste	paste	paste
Appearance	white	yel-lowish	white	white	white	white	white	white
Candidate ?	n.g.	maybe	no better	n.g.	n.g.	n.g.	n.g.	maybe

TABLE 3. COMPOSITIONS								
Solvent as ML, Oxidant & Gelling Agent Weight in Grams								
Test Serial No.	99	100	101					
KClO ₄		3.2	3.2					
NaClO ₄	3.4							
Ba(ClO ₄) ₂								
Sr(ClO ₄) ₂								
Li(ClO ₄) ₂								
Trimethylborate								
Dioxan								
Acetone								
Methanol			2.9					
Ethanol								
Pyridine								
Triethyl Amine								
Diethyl Amine								
Hexane								
Kerosene	2.2	3.0						
Mineral Spirits								
Duponol G								
Carbopol 940		1.1	0.3					
Zelec NK	1.4							
Alkanol HCS								
Hexaglycerol-disoyaester								
REMARKS:								
Ignition	good	good	good					
Propagation	good	good	good					
Color Purity	good	poor	good					
Color Intensity	strng	weak	strng					
Viscosity	paste	paste	paste					
Appearance	white	white	white					
Candidate ?	maybe	n.g.	maybe					

In appearance these compositions ranged from a sticky, white mass resembling rubber cement in its consistency (Ba-1) through a white substance of the viscosity of library paste (Na-1) to a yellow, soapy or semi-solid (Ba-2).

Initial tests of the mixes to measure intensity and secure spectral data were made by loading them into aluminum foil or red fiber cases, to secure a reasonably constant burning rate and flame shape by restricting combustion of each mix to a comparable surface. The Ba-1 mix, when loaded into such a foil case of 1/2 inch I. D. and ignited, burned steadily with a brilliant green flame. Combustion proceeded evenly, just as in the typical solid pressed NaNO_3 -Mg flare mixes. On the other hand, Ba-2 burned with a smoky flame typical of kerosene which was interrupted by bursts or pulses of brilliant green light. This same pulsation occurred with the Na-1 mix, the flame during "rest" periods being almost invisible. Further studies of the combustion processes may account for the mechanism of this pulsation, but were not attempted in view of the time they would have taken from work on the main objective. Measurements of the intensity, dominant wavelength and color purity were greatly hampered by the pulsations. Of the results obtained from these mixes those from the Ba-1 mix were the only ones that could be reduced with confidence in the results. As a result of later requirements that made different physical properties desirable, some related but different compositions were used and data has been obtained from some of these, also. The results obtained from typical burns are shown in Table 4.

The maximum peak intensity produced in these tests by burning 5 gms. of Ba-1 mix in an aluminum case was approximately 2000 candela. The Na-1 mix under similar conditions produced a maximum peak reading of 675 candela. No value was obtained from the Sr mix because of low readings. It is interesting to note that this sodium mix produced an intense, orange-colored flame rather than the typical yellow. Furthermore, when the room was viewed through didymium glasses it was seen to be brightly illuminated by this flare. It is well known that the transmission of didymium glass is quite low, depending on its thickness, in the spectral region from 5750 Å to 5950 Å. It will not transmit the sodium D-line radiation to any appreciable extent when the glass is two or more millimeters thick, yet the light from this sodium flare is quite brilliant when viewed through this thickness of it. The phenomenon is thought to be another example of sodium line-broadening. The broadening is seldom seen in small flares and is considered to be a good indication of the effectiveness of this gel as an illuminant, because it indicates that radiation of visible energy is being accomplished with much more efficiency than could be expected from atomic line radiation alone.

Spectra were taken of these flames with the B & L 1.5 meter spectrograph. Typical results are shown in Appendix A, Plate 1, for a NaClO_4 - CH_3OH mix burned in a.) a red fiber tube, b.) an aluminum foil tube and c.) in a cardboard tube. In the latter case, 5% by weight

TABLE 4.COLOR AND LUMINOUS INTENSITY OF TYPICAL PERCHLORATE-METHANOL GELS.

<u>Mix</u>	<u>Casing</u>	<u>Dominant Wavelength Microns</u>	<u>Purity %</u>	<u>Candela</u>
Ba-1	None	555	68	145
IV-a	Al-foil	520	16	2745
IV	Al-foil	560	28	1400
II	Al-foil	606	72	675
V	None	620	97	14

Note: Ba-1 Methanol, 29%; Ba(ClO₄)₂, 71%; Carbopol, 3% by wt. of mix.

II Methanol, 33%; Na(ClO₄)₂, 79%; Carbopol, 2% by wt. of mix.

IV Methanol, 21%; Ba(ClO₄)₂, 79%; Carbopol, 2% by wt. of mix.

IVa Methanol, 20%; Ba(ClO₄)₂, 75%; Carbopol, 3 % by wt. of mix.

V Methanol, 32%; Sr(ClO₄)₂, 68%; Carbopol, 2% by wt. of mix.

of Mg powder had been added to the gel. This was to provide a basis for more directly comparing the gel spectra with the spectra of magnesium-fueled pyrotechnics. The spectra in Plate 2 are from $\text{Ba}(\text{ClO}_4)_2\text{-CH}_3\text{OH}$ gels burned in a.) an aluminum foil tube, b.) an "Inconel" tube and c.) of the same mix with 5% of Mg added burned in an aluminum foil tube and d.) without any container at all. It is apparent that the spectra from the $\text{NaClO}_4\text{-CH}_3\text{OH}$ gels are essentially identical. The continuum that is evident in all three flames is believed to be due to sodium atoms in high concentration and at relatively high temperatures. The flame is so bright when viewed with the unaided eye as to be dazzling; however, the readings of candela do not support the physiological sensation of brilliance.

The $\text{Ba}(\text{ClO}_4)_2$ gel spectra also show no effects that can be attributed to the type of container or to the presence of small amounts of 200 mesh magnesium powder in the gel. In general, the extensive band structure that is attributed to BaO is very prominent, as are the BaCl bands in the 5000 Å - 5500 Å region.

The spectra appear to be rather typical of the flame spectra produced by these metals in high temperature oxidizing flames. It is surprising that the atomic lines of magnesium at 5167 - 5183 Å and at 3830 - 3838 Å and the bands of MgO at 3815 Å, 4974 - 5007 Å and 5778 Å do not appear in these spectra. These additions of magnesium were made for the purpose of introducing solid particles of MgO into the flame, in order to obtain a direct comparison of color purity between essentially similar flames with and without solid radiators. I. e., one was to contain solid thermal radiation emitters as well as the molecular and atomic emitters, while the other contained only the molecular and atomic emitters. Since a result useful for this comparison was not obtained from a reasonable amount of effort, using up to 10% Mg, this question was not pursued further.

Some work was also done at this time to investigate the possibility of using single or combination jets of air-reactive materials, sprayed under pressure into the atmosphere, as illuminating or signaling sources. This was the result of a feeling that sodium might be utilized more directly and efficiently as an illuminant by this technique. A stainless steel "bomb" type of container was fitted with a fog nozzle and loaded with a solution of approximately 5 gms. of sodium metal in 50 ml. of liquid NH_3 . This dark-blue, somewhat viscous solution develops a vapor pressure of about 800 p.s.i. at room temperature. It was hoped that when a solution of metallic sodium in liquid ammonia was sprayed through a fog nozzle into the air that the particles might be pyrophoric. This was not the case. It was then sprayed into a variety of gas-oxygen flame geometries in an attempt to obtain the desired radiation from the sodium atoms. The spray velocity was apparently too high and the

dwelt time of the Na in the flame too short for an effective exchange of energy to occur. The average temperature of the Na is assumed to have been too low, so that little radiation could be produced. Since the velocity of the spray is directly a function of the pressure, a reduction in pressure was sought to increase the dwell time. This was obtained by dissolving sodium in diethylamine and using argon to pressurize the ullage space in the bomb to 1 to 5 p.s.i. Much better results were produced, in luminosity, when this spray was directed through a fuel-poor propane-oxygen, vortex flame. However, the flame temperature still should be higher and the dwell time or mixing with the flame much improved to excite the sodium continuum. A solution of sodium perchlorate in methanol was tried in place of the diethylamine solution in an attempt to secure higher temperatures, but results were disappointing and this line of investigation was dropped and the effort returned to the study of the gelled perchlorate-alcohol compositions.

The top was removed from one of the MK 2-0 Markers and a means for connecting it to a source of acetylene gas was provided to supply gas to the orifice from which the flame appears during operation. From the earlier work it was known that the acetylene in the marker is generated at a pressure varying from roughly 4" to 6.5" of water and that it is vented through an orifice of about 0.062" diameter. A flowmeter and water manometer were connected to the acetylene supply and the flow monitored as the pressure was adjusted over the range from 0.5 inches to 9.5 inches of water. The results obtained from the flames produced are shown in Table 5. These values of candela and supply pressure have been plotted in Figure 1. The flame first tends to increase in length much more than in width as the pressure is increased, later becoming bushier but not much longer.

A device to inject the gelled composition into the flame was next designed. This passed through several stages in successive efforts to secure the desired effects. Although a gelled perchlorate-alcohol mix when placed on a fire-brick or metal block can be ignited quite readily with a match, the same material will drip through an acetylene-air diffusion flame without ignition. The problem this causes may be visualized from Figure 2, which represents the general configuration of the injectors, and Figures 3 and 4 which are photographs of the parts of an injector.

The mix, extruded from the storage volume by the pressure of the methanol vapor, passes into the central zone. The flame is burning in this region and essentially fills it completely. The gel material will drip down through the central aperture to the jet support plate below. Hence, it will eventually cover the jet and there is little or none of the desired action on the flame during the time that this whole process is taking place. It also appeared that the con-

TABLE 5.

CHARACTERIZATION OF ACETYLENE DIFFUSION FLAME IN AIR

Gas Pressure Inches H ₂ O	Flow, in ³ /min.	Flame Height inches	B.T.U./min. input *	Candela per B.T.U./min.	Average Candela measured
0.5	22	5.5-6	19	--	--
1.0	43	6.5-7	36	0.25	9.2
2.0	68	8	58	0.26	15.
3.0	87	9	76	0.28	21.
4.0	102	9-10	87	0.36	32
5.0	123	10-11	106	0.37	40
6.0	135	12	124	0.51	59
9.5	167	--	143	--	--

Note: Diameter of the orifice supplying acetylene is 0.063 inches.

* Calculated as in³ /min acetylene supplied; assumed all burned and supplying 0.86 B.T.U./in³ .

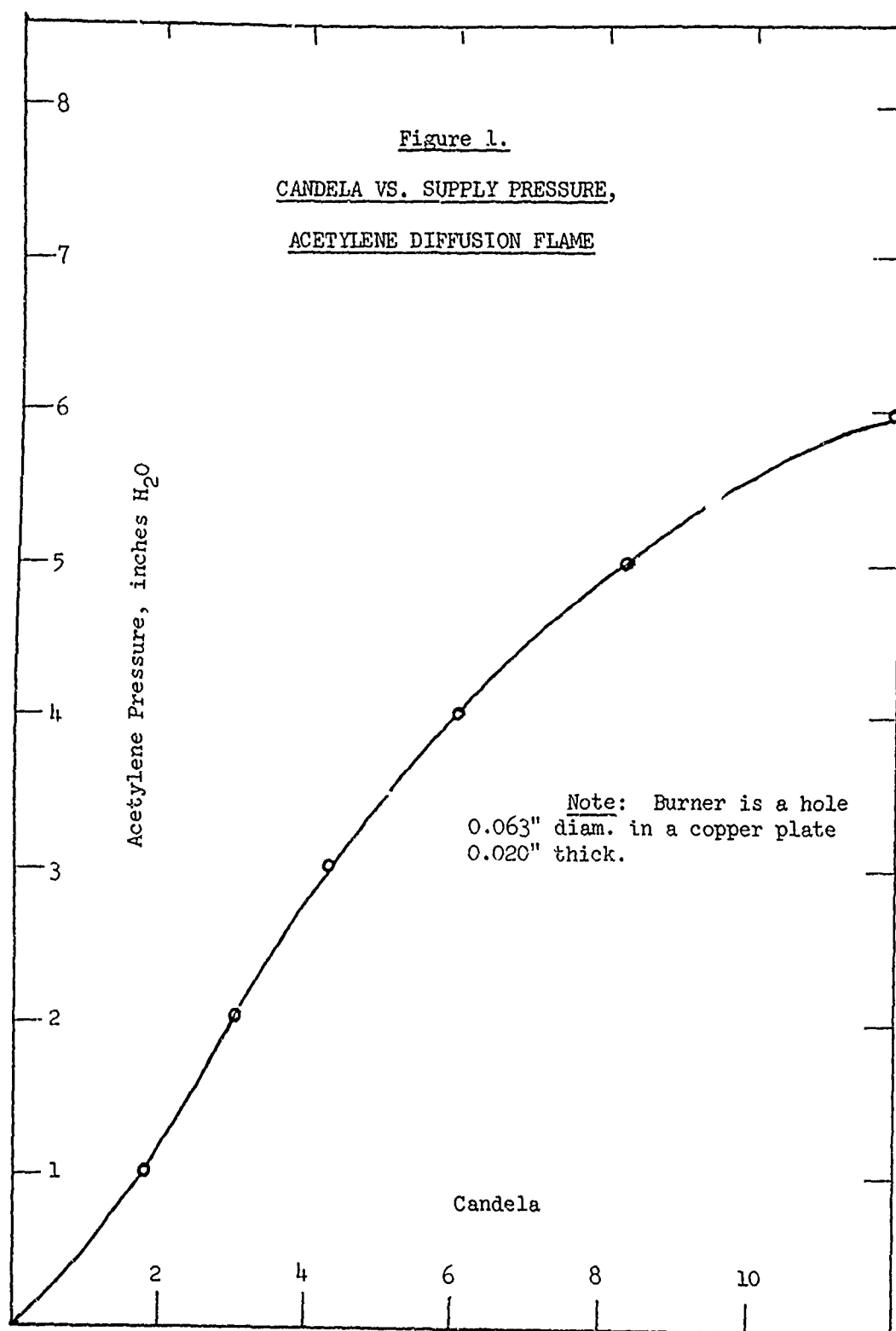
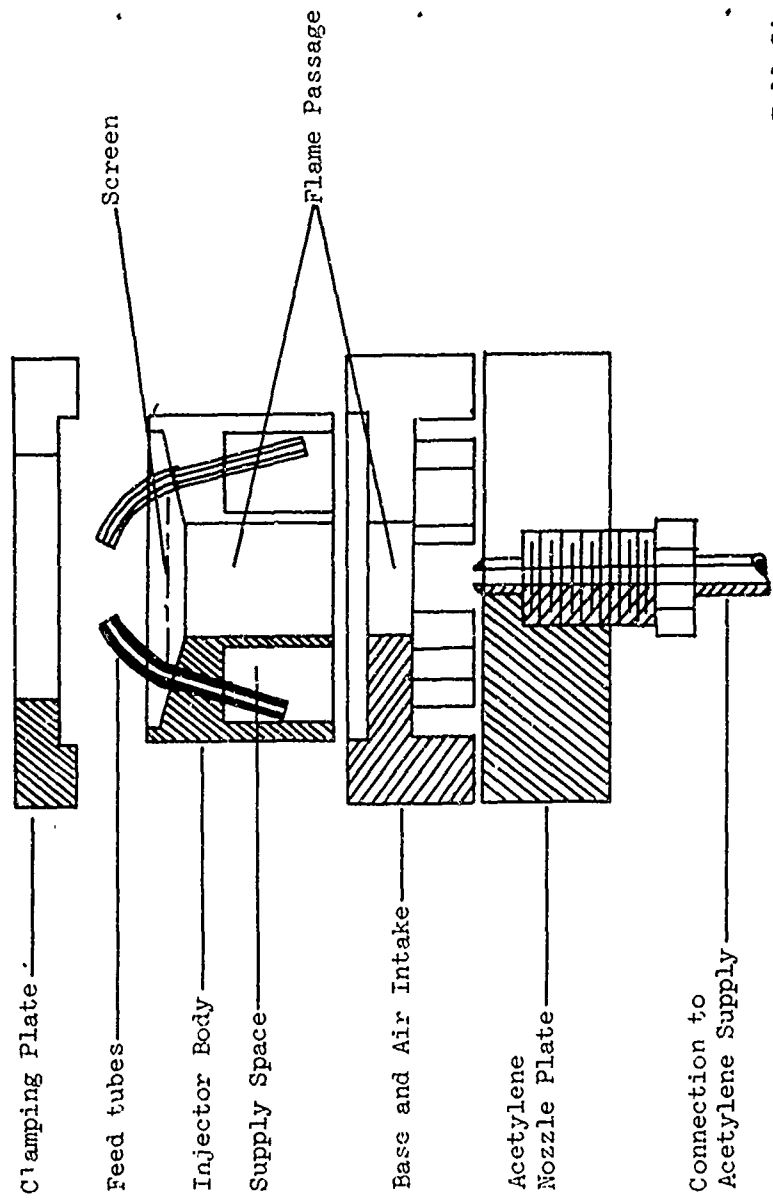


Figure 2.

Cross Section of Gel Injector



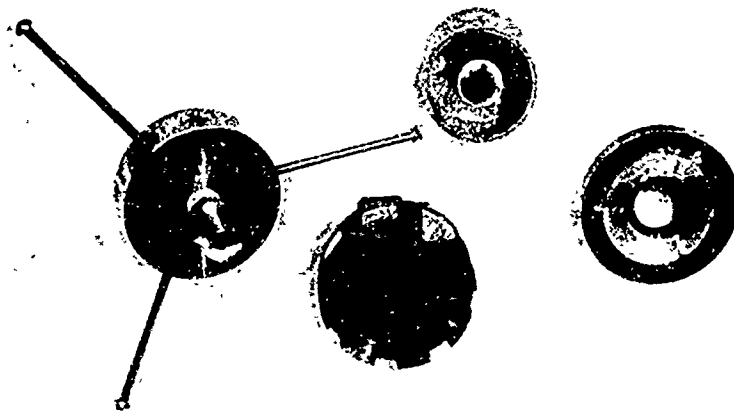


Figure 3.

View of Gel Injector Components from the Bottom.

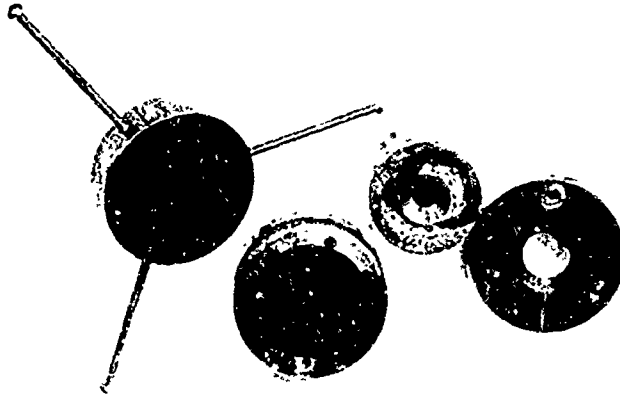


Figure 4.

View of the Gel Injector Components from the Top.

struction of the injector allowed too much heat to reach the passages that fed the material to the flame. Thus the solvent, being evaporated by this heat while the mix was still in the supply passage, would leave a residue containing an excessive quantity of oxidizer. This mix would not burn properly and might even lead to clogging of the feed tubes. The injector design was modified to reduce the heat input to the feed tubes and a screen was placed across the flame to catch the extruded mixture. This was done to maintain it in a flame region of higher temperature that should ignite the mixture and also to keep it out of the gas supply nozzle.

The first attempt to use the modified burner was made with a sodium perchlorate-methanol gel and was only partially successful. The mix was forced out of the supply tubes into the flame zone as expected. However, it accumulated there until approximately 2 grams were piled on the screen. This quantity suddenly ignited and burned rapidly, with the orange flame typical of this mix. During this time the visible output from the acetylene flame was completely suppressed and replaced by that from the burning gel. Since the ignition was so long in occurring and the combustion of the material occurred in an undesired manner, further modification was made.

This modification produced a wider spread of the gel on the screen but also resulted in early clogging of the end of the feed tube that was heated in the flame. Most of the material was held back by the clogged tubes and never reached the flame. A lower viscosity mixture was then tried in an attempt to eliminate the clogging, but was not successful.

IV. DISCUSSION AND CONCLUSIONS

The application envisioned when this study began was that of providing a gel that would act as a source of additional oxygen when extruded into a flame such as that from the MK 2-0 Marker. Coloration of the flame for identification was an added capability. The current study indicates that more work will be required to overcome the problems encountered than could be done in the present contract. It has not been possible to bring the development of the gelled perchlorate-alcohol type of pyrotechnic composition and the associated hardware to the point at which it can be demonstrated as an additive to the flame produced by an operational device such as the Marker, Marine, MK 2-0. It has been shown that this material promises a new approach to the design of pyrotechnic devices. It also would be desirable to investigate a new device, designed from the start to use the gelled mix as the major source of light. Ignition and re-ignition in the new design could be based on the techniques, and materials discussed by Ripley in his investigation of air and water reactive materials¹². Further work is needed to determine the reason for the ignition behavior of these gels. That is, the apparent anomaly presented by the ease with which the gel is ignited by a match or soft bunsen flame, contrasted with the difficulty in igniting it with the acetylene-air diffusion flame. This problem is really at the root of the failure to adapt the MK 2-0 Marker to use the gelled mix as an additive to the flame.

The fact that the measurements of candlepower do not reflect the dazzling intensity the burning gel presents to the eye is not completely understood. It may be that the major source of visible radiation is a very small area of quite high luminance, perhaps representing a high temperature reaction zone. This condition would produce a relatively low value of candela, appropriate to the luminance and area of the reaction zone. The eye, however, would be dazzled by the passage of a narrow cone of high intensity radiation through its structure as the intensely brilliant spot is focused on the retina. Since this composition has physical properties that are different from the customary pressed or cast mixtures, a new approach to the design of pyrotechnic devices could be taken when the materials properties are better understood. It appears that work should be done to study this "dazzle" effect with the aim of establishing its cause, because it may be evidence that a new, intense source of illumination can be produced by causing the observed reaction to occur over a larger area of the composition. This would provide an alternate for use in place of the $Mg-NaNO_3$ compositions.

Finally, some indications have been found that the amount of water present in the raw materials can affect the luminance and combustion

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of the gel more than would be anticipated. The indications are at present no more than the intuition of the investigator based on a few experiments, but it is felt that further work on these gels should recognize the possibility that close control of raw material may be essential to good results.

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APPENDIX

A. FLAME SPECTRA

Plate 1 -- NaClO_4 gel

Plate 2 -- $\text{Ba}(\text{ClO}_4)_2$ gel

B. FLAME CHROMATICITY

Plate 3 -- Chromaticity of Gels

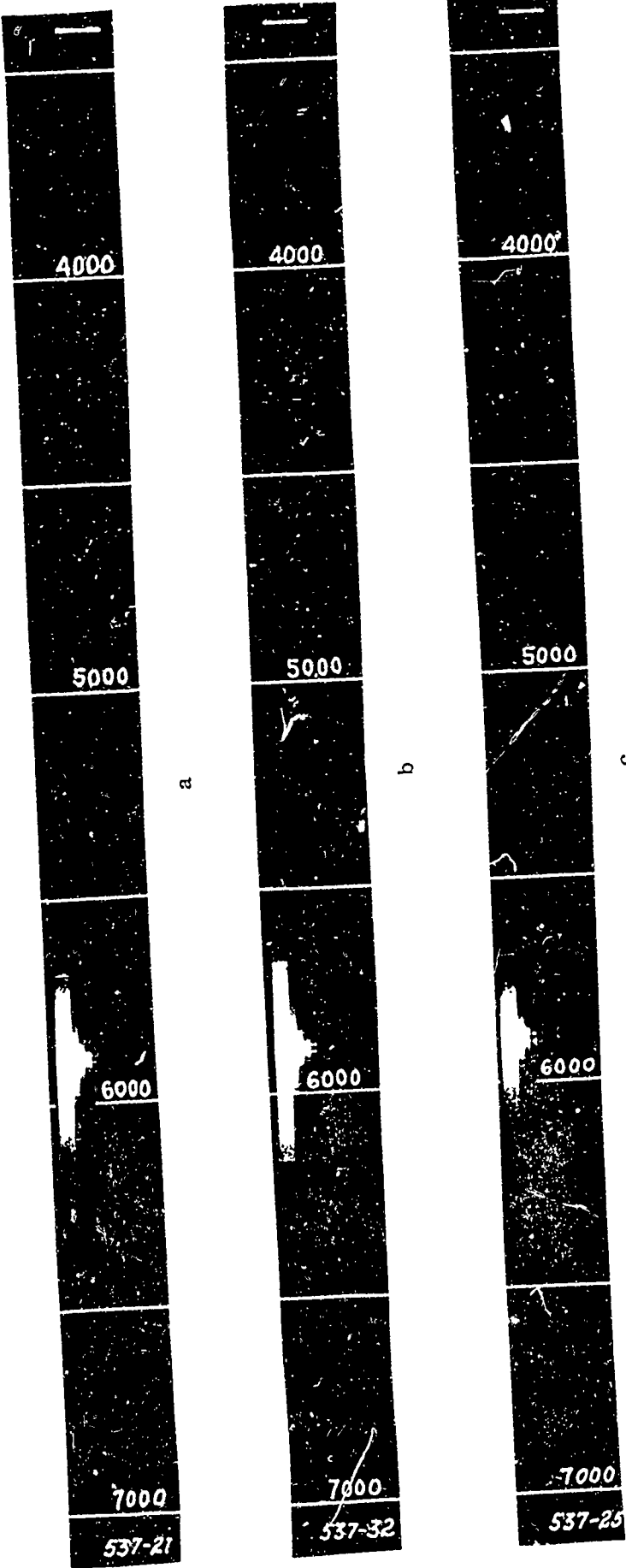


PLATE 1



a



b

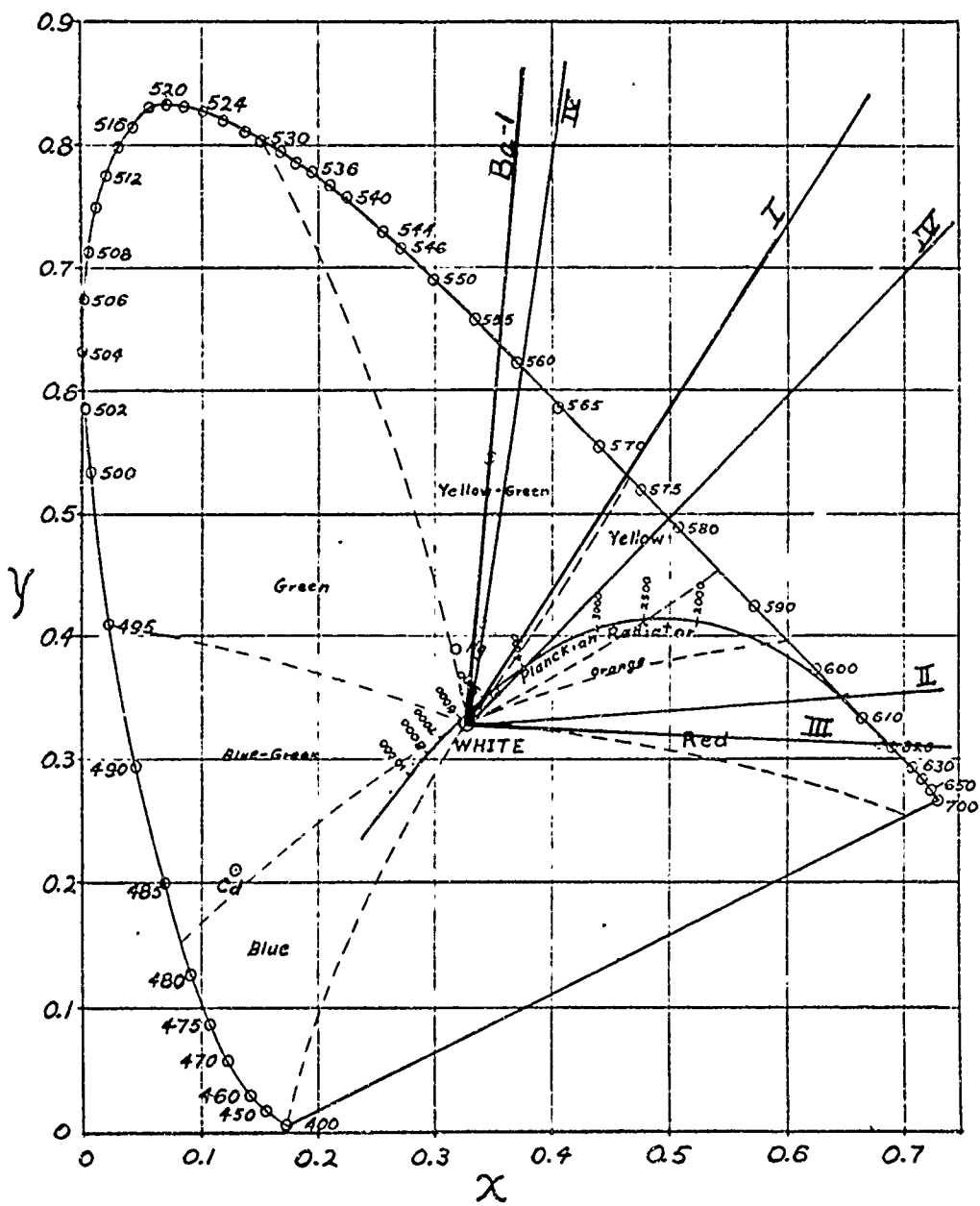


c



d

PLATE 3.
CHROMATICITY OF GELS



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Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) Denver Research Institute University of Denver Denver, Colorado 80210		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP ---
3. REPORT TITLE Study of Gelled Illuminant Compositions		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report May 1967 - May 1968		
5. AUTHOR(S) (First name, middle initial, last name) Robert M. Blunt		
6. REPORT DATE 23 May 1968	7a. TOTAL NO OF PAGES 33	7b. NO OF REFS 12
8a. CONTRACT OR GRANT NO	9a. ORIGINATOR'S REPORT NUMBER(S) Final Report 3537-6805-F	
b. PROJECT NO AIRTASK No. 435-532-022/323- 1/F008-17-02 Work Unit No. 15		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) NAD Crane RDTR 116	
d. NO0164 - 67 - C - 0498		
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Naval Ammunition Depot Crane, Indiana, 47522	
13. ABSTRACT The high luminous intensity and color purity produced by the flames resulting from the combustion of Group II perchlorates with alcohol and other organic solvents had been noted in a 1966 study of air and water reactive materials (1). This present study was to investigate the feasibility of using these mixtures in markers, flares and similar devices or units that could be dropped from an aerial landing unit. The approach taken was that of characterizing the flame produced by a typical, operational device, which was the Marker, Location, Marine MK 2-C, Depth Charge, Night, in terms of size and candela. The intention was to show the improvement resulting from the addition of perchlorate-fuel gels to this flame, using a prototype of a device that might be added to existing markers of this type. It is concluded that a redesign of the marker would be necessary to take advantage of the properties of this particular gelled oxidizer/fuel combination. Data on gelling agents, Group II perchlorate solubilities in various organic liquids and flame color and candlepower are reported.		

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S/N 0101-807-6801

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Flares Gels Perchlorates Colored Flares Illuminating Flares Markers, Marine Flames Emitters Spectra						

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